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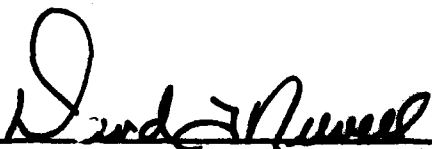This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-82-C-0083 with the Space Division, Deputy for Technology, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by S. Feuerstein, Director, Chemistry and Physics Laboratory. 1st Lt Efren V. Fornoles, SD/YLXT, was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) Program.
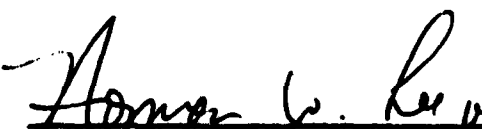
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The charge efficiency of the nickel-cadmium cell is found to be 100% up to the state of charge where oxygen evolution begins to take place. Inefficiencies at lower states of charge are due to poor utilization of capacity on discharge rather than to any inefficiency in rechargability. The dependence of the utilization efficiency on charge and discharge rates is reported. The results are consistent with the hypothesis that the utilization of capacity in the nickel electrode is limited by the formation of a depletion layer at the current collector-active material interface.

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CONTENTS

FIGURES

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I. INTRODUCTION

Efficiency measurements for nickel-cadmium (Ni-Cd) cells generally combine the effects of poor charge utilization during discharge with the charge inefficiencies that result from oxygen (O_2) evolution during recharge at the Ni electrode. Charge efficiency in this sense refers to the percentage of charge input that is electrochemically stored in the cell, while charge utilization refers to the percentage of electrochemically stored capacity that is returned under specific conditions of discharge. Charge efficiency and utilization are often difficult to evaluate separately, because they are both important in typical measurements that involve determining the capacity output as a function of input.

Previous reports of both integrated and differential (incremental)[1,2] charge efficiencies generally include the effects of changing charge utilization as well as variations in charge storage efficiency. Such reports of charge efficiency do not provide good data at states of charge less than 20% of full 'charge. The reported data at low states of charge are usually erratic, a result that has typically been attributed[1,3] to an inherently nonreproducible charge acceptance at low states of charge. At low states of charge (voltages well below the O_2 evolution potential), no electrochemical or chemical reactions have been proposed that could give rise to significant inefficiencies in charge acceptance. Therefore it is likely that any nonreproducibility in apparent charge acceptance at low states of charge results from variations in the utilization of stored charge. Nonreproducibility in such utilization is most likely caused by variability in test conditions.

This report presents a study of charge efficiency and charge utilization for Ni-Cd cells, particularly in the low state-of-charge region. Precise and reproducible control of the immediate cycling history, charge and discharge currents, charge and discharge times, stand times, and temperature are incorporated in the experiments, since all these parameters are expected to affect utilization at the lower states of charge. The results will be used to evaluate the chemical processes that influence capacity utilization during Ni-Cd cell discharge.

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II. EXPERIMENTAL PROCEDURES

All the measurements reported here were made on several 10 Ah sealed Ni-Cd cells manufactured by General Electric. The cells had polypropylene separators. Cell charge and discharge intervals and currents were computer controlled, and cell voltage was continuously monitored by the computer. A programmable power supply (Kepco 36-5M) was interfaced to the computer, and was used to charge and discharge the cells. Cell temperature was controlled at 23 ± 0.1°C in a thermal bath.

Prior to each measurement cycle the cell was charged and discharged 5 times by means of a standard cycle consisting of charging for 1000 s at 2.5 A (C/4), then discharging at 4 A to 1 V, followed by discharge at 1 A to 0.01 V. The initial cycles were intended to conveniently establish a reproducible standard for the initial state of charge. The overall charge efficiency or utilization was then obtained by recharging the cell to the desired state of charge, followed by discharge to the initial state of charge (1 A to 0.01 V).

III. RESULTS AND DISCUSSION

Figure 1 indicates typical charge efficiency and utilization profiles. Two plots are presented here, the coulometric output as well as the change in coulometric output (differential or incremental efficiency) as a function of coulometric input. The differential curves are simply the slopes of the coulometric output curves. The solid curves in Fig. 1 indicate the coulometric output for discharge at C/2.5 to 1 V, while the dashed curves indicate the output when the cell was discharged to 0.01 V through a 0.25-Ω resistor. The falloff of both curves above 40,000 C of charge input is due largely to the onset of O_2 evolution as the cell reaches full charge. The dashed lines are not substantially affected by poor utilization of the electrode capacity, since the capacities were obtained by means of a low rate, deep discharge. Therefore, the dashed lines in Fig. 1 provide a good indication of charge efficiency, which is 100% up to about 40,000 C (111% of rated capacity), after which the charging efficiency drops off to zero as a result of the onset of O_2 evolution in overcharge. The solid curves are an indication of usable high rate capacity, and therefore include inefficiencies arising from poor capacity utilization as well as from O_2 evolution.

The data in Fig. 1 indicate two regions that contribute to poor charge utilization. At high states of charge it appears that continued overcharge past the region where the charge acceptance approaches zero results in a loss of capacity utilization. Such a falloff in charge acceptance is likely to result from the active material in the Ni electrode being charged into a phase or an oxidation state that is more difficult to discharge at high rates[4] but is discharged effectively at lower rates. At low states of charge (lower than about 25% of rated capacity), the utilization of charge is also rather poor. It is in the low-capacity region that little data exist on the factors that affect charge utilization.

The variation in differential utilization efficiency for different discharge rates is indicated in Fig. 2, where a 2.5-A charge rate was employed. The data show that up to about 25% of the capacity stored in the Ni electrode of these cells may be poorly utilized at higher discharge rates. At sufficiently low discharge rates the utilization is high even at very low states of charge. The data illustrate that the processes that control
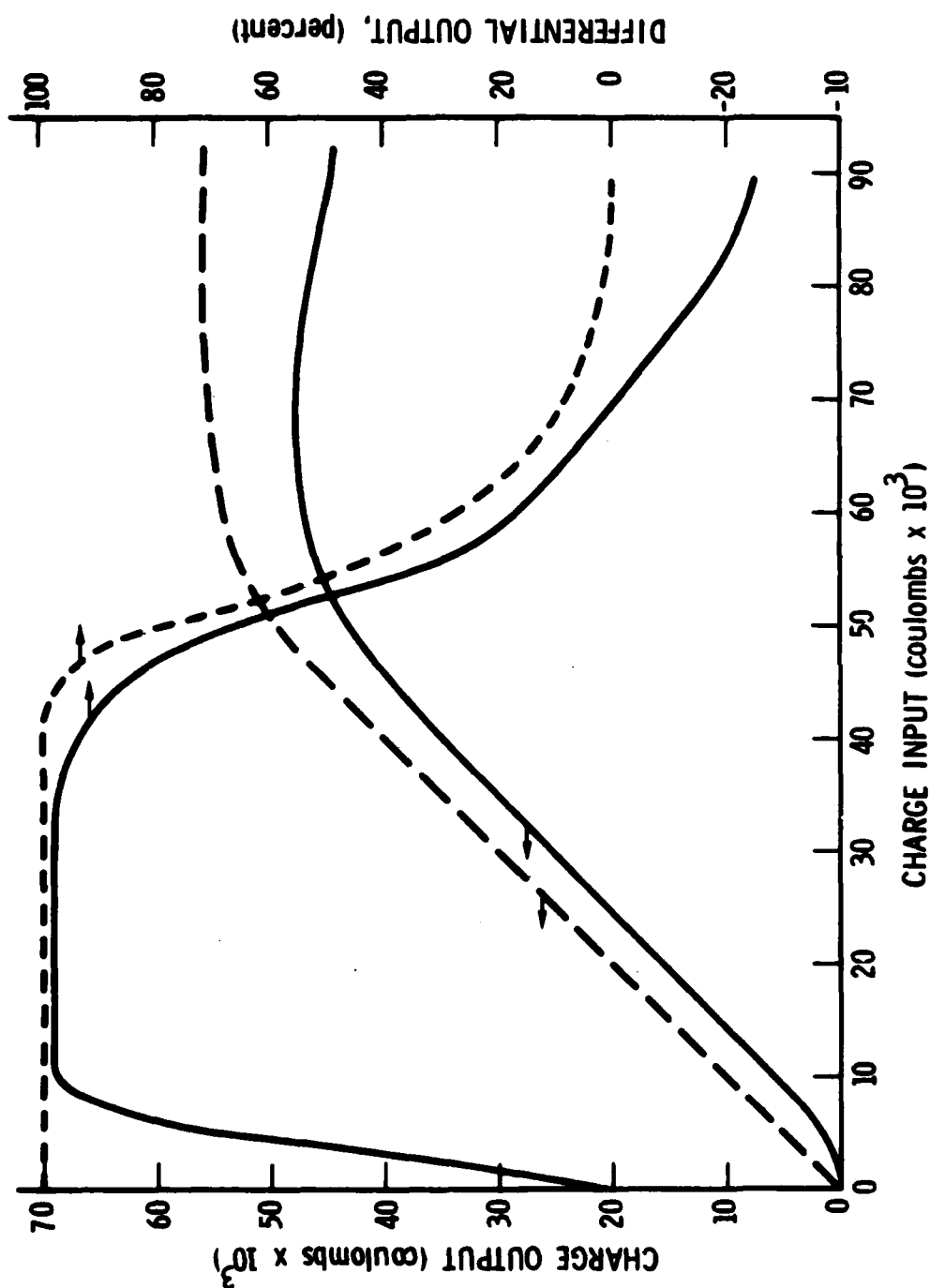
Fig. 1. Capacity Output and Differential Efficiency as a Function of Charge Input for C/2.5 Discharge Rate (solid line) and Discharge to 0.01 V through 0.25-Ω Resistor (dashed line). Charge was at C/4 rate up to 36,000 C input; above this the charge rate was C/10.

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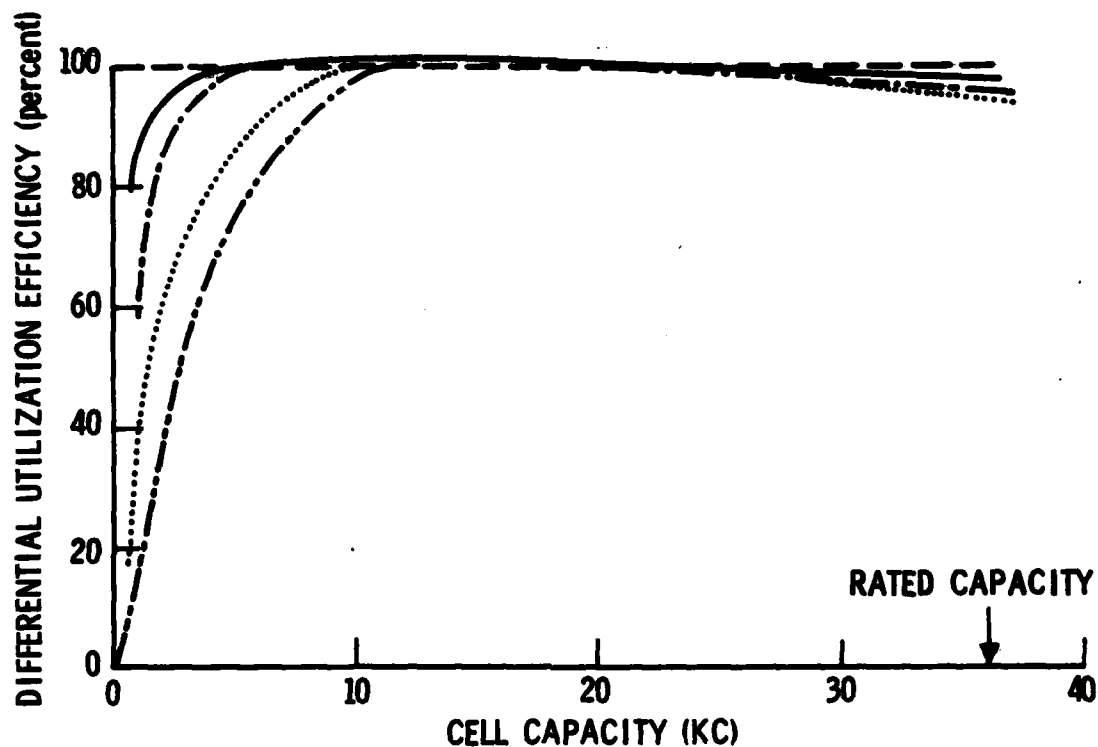
Fig. 2. Capacity Utilization Efficiency as a Function of State of
Charge for Different Discharge Rates: 0.2 A (dashed
line), 0.5 A (solid line), 1 A (dash-dot line), 2 A
(dotted line), and 4 A (dash-dot-dot line). The
coulombic output was measured to a cell voltage of 1 V.
The charge rate was 2.5 A. Prior to each efficiency
measurement the cell was subjected to 5 standard charge-
discharge cycles to stabilize performance.

utilization at low states of charge are particularly sensitive to discharge rate.

The effects of varying charge rate on the utilization efficiency are indicated in Fig. 3 in the low state-of-charge region. The use of higher charge rate provides a significant improvement in utilization. The data in Fig. 3 suggest that the best capacity utilization is realized when the cell is initially charged at a high rate, and that the charge rate should then be decreased to a lower value after the cell is charged at least 50%. This procedure assures that the best utilization of the capacity is returned during recharge, while avoiding the degradation associated with high-rate overcharge.[5]

The capacity utilization was also found to depend in an interesting way on the previous cycling history of the cell. The efficiency of utilization for the first 2500 C of recharge was taken as a measure of utilization at low states of charge. In Fig. 4 the initial utilization is plotted as a function of the highest state of charge that the cell reached during the previous cycle. Before each of the experiments in Fig. 4 was begun, the cell was shorted down for 16 h through a 1-Ω resistor, recharged for 16 h at C/10, and discharged at 4 A to 1 V then at 1 A to 0.01 V. Thereafter, before the cell was brought up to a given state of charge by means of a 2.5-A charge rate, 5 standard charge-discharge cycles (2500 C returned) were done to stabilize performance. Figure 4 indicates that as the state of charge from which cell is discharged increases, the initial utilization upon recharge decreases. This effect is much more pronounced at higher discharge rates, as shown in Fig. 4.

The results in Fig. 4 indicate that discharge from a relatively high state of charge leaves the active material in the Ni electrode in a condition that is subject to relatively poor utilization after recharge. The apparent difference in the state of the active material, depending on how high a state of charge it has been discharged from, suggests that the charge voltage may show a systematic variation as the chemical nature of the active material varies. A variation in charge voltage is indeed obtained, as indicated in Fig. 5. The charge rate in Fig. 5 was 0.2 A, and after each charge period the cell was discharged at 4 A to 1 V, at 1 A to 0.01 V, then cycled 5 times to stabilize performance by means of a 2500-C standard recharge. The cell was

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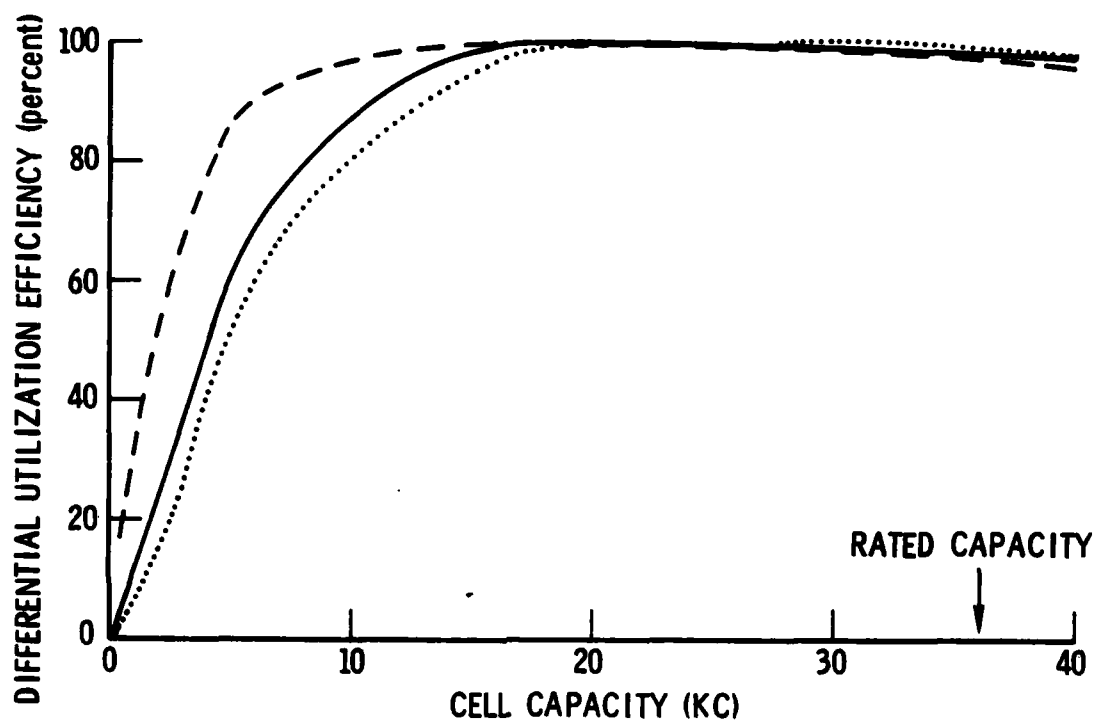
Fig. 3. Capacity Utilization Efficiency as a Function of State of
Charge for Different Charge Rates: 0.2 A (dotted line),
1 A (solid line), and 2.5 A (dashed line). The discharge
rate was 4 A, each discharge being to 1 V. Prior to each
efficiency measurement the cell was subjected to 5
standard charge-discharge cycles to stabilize
performance.
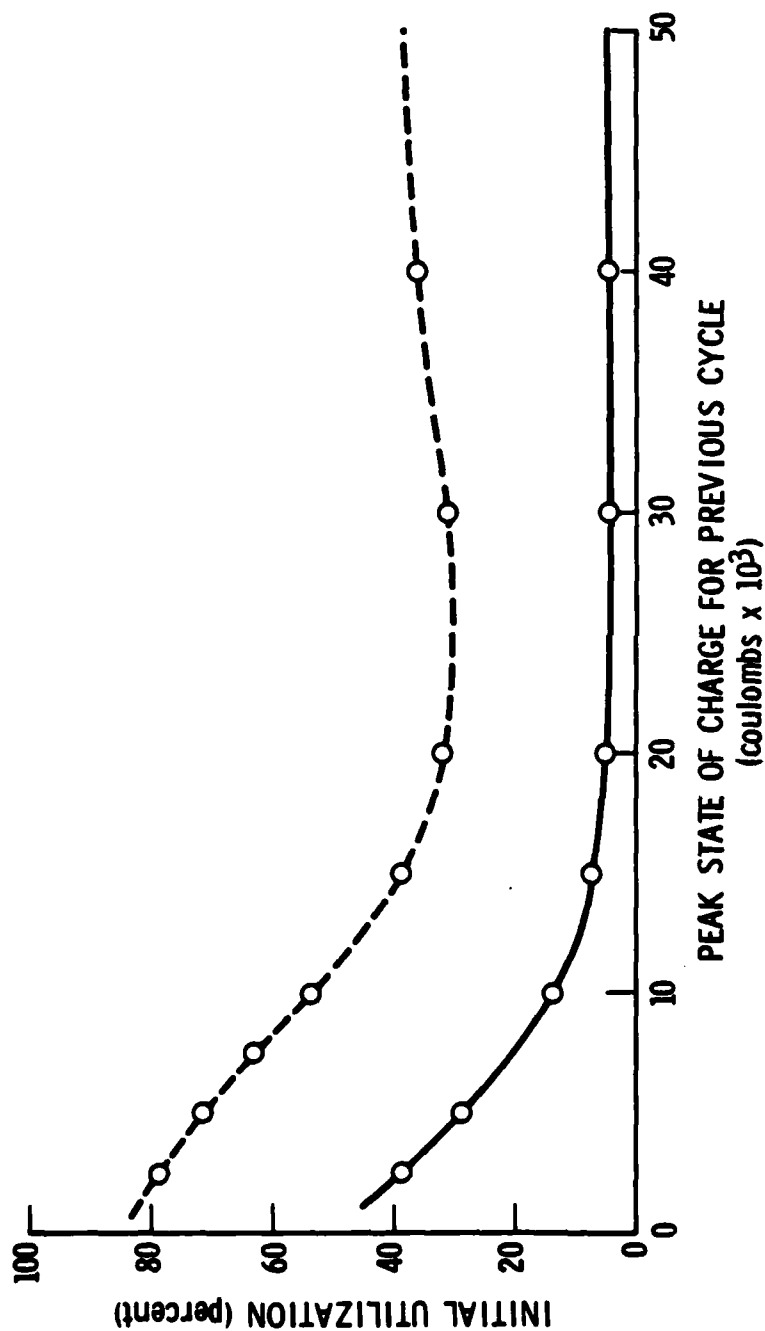
Fig. 4. Initial Capacity Utilization as a Function of the Prior State of Charge from Which the Cell Has Been Discharged. The initial utilization is an integrated efficiency over the first 2500 C of recharge at 2.5 A following discharge. The dashed line is for a 1-A discharge to 1 V, the solid line for a 4-A discharge to 1 V.
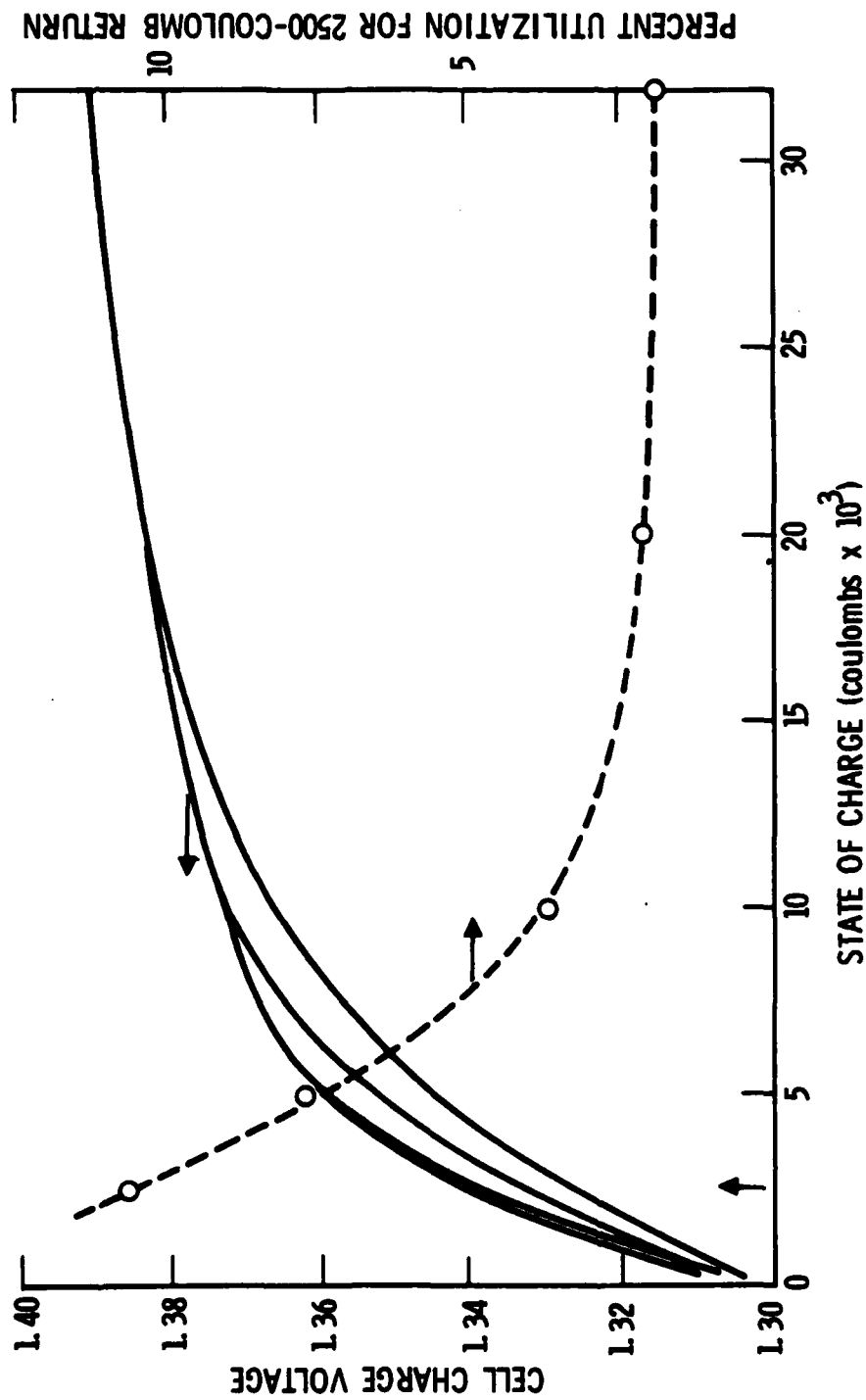
Fig. 5. Charge Voltages during 0.2-A Recharge. Between each of the four recharges indicated, the cell was completely discharged and cycled 5 times by means of a 2500-C recharge. The recharges indicated were done in the order of increasing charge return. The utilization for a 2500-C charge return after each discharge is also plotted as a function of the state of charge reached during the prior recharge.

first recharged to 5000 C, then was discharged so that the utilization efficiency could be obtained and the cell could be returned to the standard discharged state. (Using a 1-A discharge to 0.01 V discharged all capacity that had been put in during recharge.) This same procedure was then done using recharges of 10,000, 20,000, and 36,000 C. The result (see Fig. 5) is that the material discharged during the previous cycle recharges with a lower voltage, and that after the previously discharged material is recharged the voltage follows its original profile for additional recharge. The integrated utilization efficiency at a return of 2500 C (2.5-A rate) is also plotted in Fig. 5 as a function of recharge on the previous cycle, and indicates that the efficiency of capacity utilization at low states of charge falls off as the initial recharge voltage decreases. The results in Figs. 4 and 5 again point out that the state of the active material in the Ni electrode depends on the manner in which the electrode is cycled, primarily on the range of state of charge involved and the charge and discharge rates.

IV. A PROPOSED MECHANISM FOR UTILIZATION AT LOW STATES OF CHARGE

Although the data reported here clearly show that changes that affect charge utilization can take place in the active material at the Ni electrode (in a positive-limited Ni-Cd cell), these data alone do not clearly indicate a mechanism explaining why charge utilization varies as it does at low states of charge. However, it is desirable to define the physically reasonable mechanisms that are consistent with the data reported here and in the literature.

As the Ni electrode is discharged at a high rate, the amount of the charge that may be utilized is controlled by the manner in which active material depletion develops at the electrode interfaces. Depletion is likely to occur at either the interface between the electrolyte and the active material, or the interface between the current collector and the active material. Since the divalent $Ni(OH)_2$ formed during discharge is not highly conductive, it seems more reasonable to assume that depletion of the Ni electrode occurs by the formation of a resistive depletion layer at the current collector-active material interface. Such a layer would be characterized by a depletion of charge carriers at a given rate of electrode operation, with the result being a large voltage drop across the layer. Figure 6 schematically indicates the electrode structure relative to this layer. The point at which depletion occurs should be rate dependent, because the thickness of such a layer, or whether a layer forms at all, will be controlled by the capability of the charge carriers at the interface to carry the current, which capability depends on the rate and the carrier density. Therefore, the trend in utilization as a function of discharge rate observed in Fig. 2 is expected.

It is generally accepted that the defect structure of the active material in the Ni electrode is responsible for that electrode's electronic conductivity at low states of charge. The active material may exist in several solid-state phase modifications,[6] each phase being a solid solution. In view of this concept, if the discharged Ni electrode is recharged at a high rate, phases containing a much higher concentration of defects should be generated than if a low charge rate were used. Furthermore, the high concentration of defects should be initially localized in the region of the

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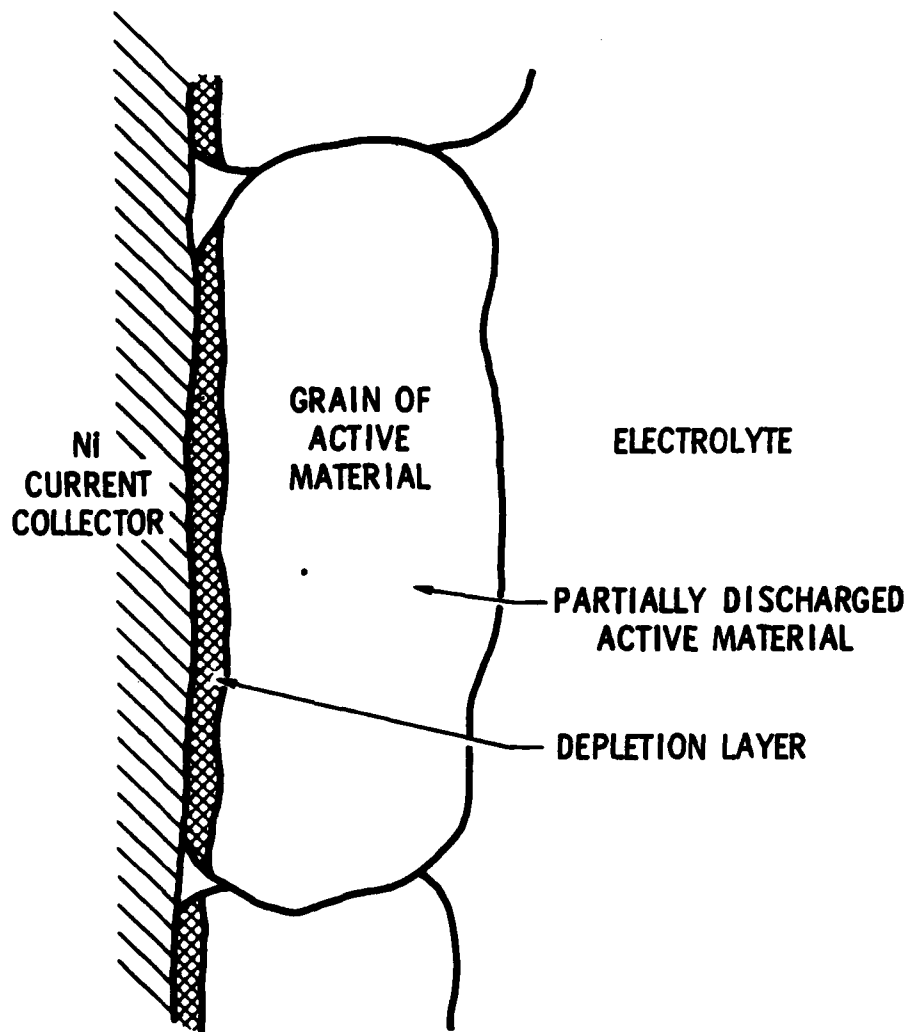
Fig. 6. Schematic Representation of the Active Material in the Ni
Electrode and the Depletion Layer That Would Limit
Utilization

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current collector-active material interface, since this is the region that was principally depleted during discharge. Such a nonuniformity in phase or defect structure would result in a higher utilization at low states of charge when higher charge rates are used, which is the trend given in Fig. 3. At higher states of charge the utilization is good because all regions of the electrode are eventually brought up to a quite high concentration of defects and high valency species.

The results indicated in Fig. 5 may be explained by the observation of Barnard et al.[6] and others that there are α and β phases of the discharged $Ni(OH)_2$. Some active material is initially discharged to the α form, which occurs at a lower potential; this gives a phase having a high defect concentration, as indicated in Fig. 5 by the lower charge voltages for this material. (Barnard et al.[6] find that discharge to α-$Ni(OH)_2$ occurs at a lower potential than discharge to β- $Ni(OH)_2$.) As the electrode is repetitively charged and discharged, as shown in Fig. 5, the charge voltage decreases for the previously cycled material, which suggests that this material has been converted to a lower potential phase. Since the lower charge voltages are accompanied by a lower initial utilization efficiency, it appears that the lower potential phase is not as readily utilized at high rates. Whether the poor utilization of the lower potential phase is due to its intrinsic lattice structure or its physical location relative to the current collector remains to be established. The data in Fig. 7 appear to indicate that during open-circuit stand or reconditioning the lower potential phase converts to a higher potential phase. The gradual voltage rise upon initiation of recharge after reconditioning in Fig. 7 is likely to be due to recovery from the deep depletion layer gradient generated during reconditioning. In the open-circuit case the depletion layer gradient is recovered from during open circuit rather than during recharge, so the voltage rises immediately when recharge is initiated.

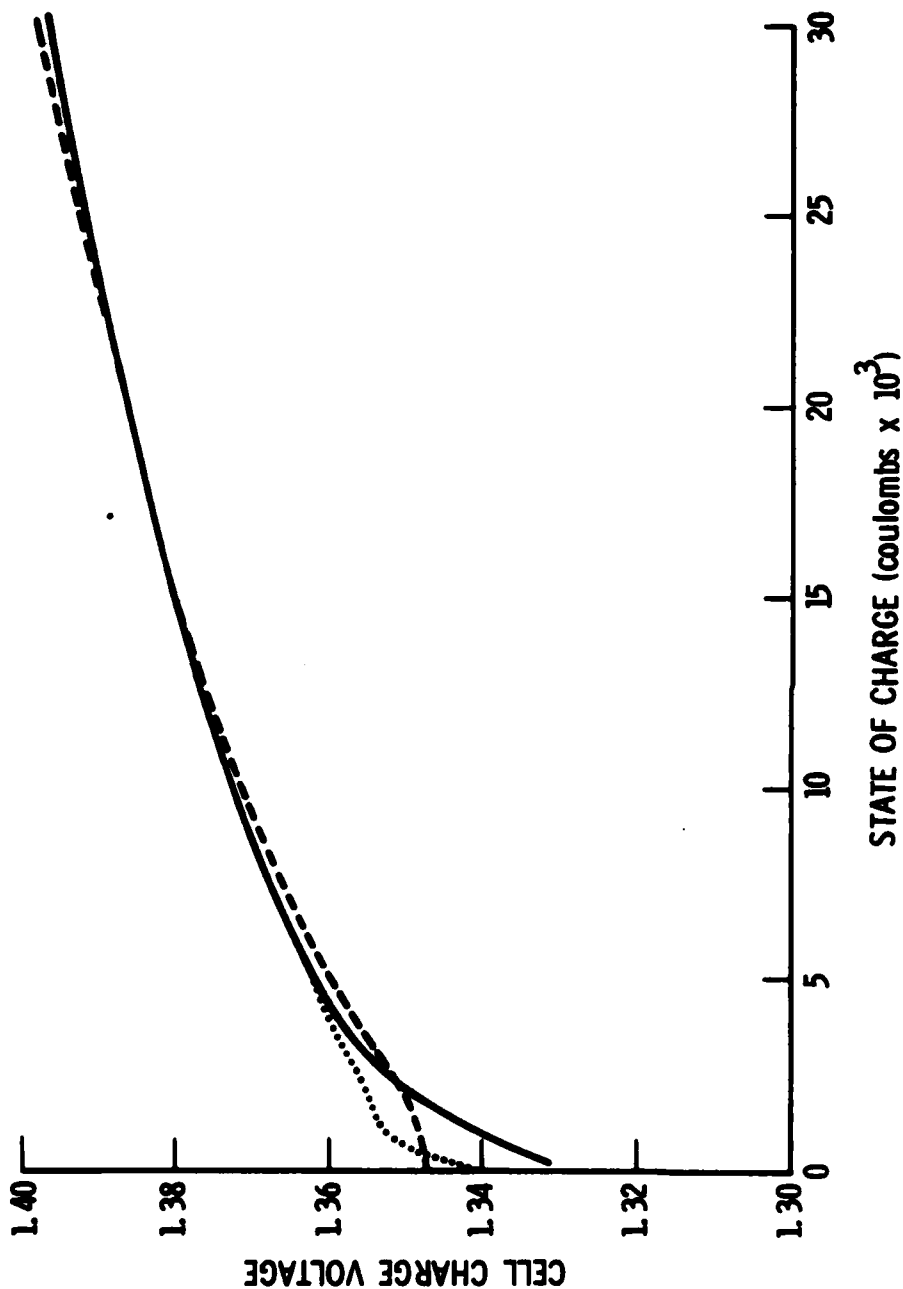Fig. 7. Cell Voltage during Recharge at 1 A for 30,000 C. The solid line indicates the charge voltage after discharge and 5 cycles to stabilize performance. The dashed line indicates the charge voltage following a discharge and a 30,000-s open-circuit stand period, and the dotted line represents the charge voltage following discharge and a 30,000-s reconditioning period utilizing a 0.5-Ω short circuit across the cell.

V. CONCLUSIONS

The Ni electrode in the sealed Ni-Cd cell exhibits a 100% charge efficiency until sufficiently high states of charge are reached that overcharge and O_2 evolution begins to take place. Inefficiencies at lower states of charge are due to poor charge utilization, which is critically dependent on discharge rate and somewhat dependent on charge rate. The data are consistent with the hypothesis that charge utilization is limited by the formation of a depletion layer at the current collector-active material interface during discharge. Evidence also indicates that active material, immediately after being discharged, is in a high defect (lower potential) phase that has lower utilization characteristics. During reconditioning or open-circuit stand, this phase appears to revert to a material having a lower defect concentration but a higher utilizability.

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